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XAS signatures of Am(III) adsorbed onto magnetite and maghemite

N Finck¹, L Radulescu¹, D Schild¹, M Rothmeier¹, F Huber¹, J Lützenkirchen¹, T Rabung¹, F Heberling¹, M L Schlegel², K Dideriksen³, S Nedel³, H Geckeis¹

¹ Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), P O Box 3640, D-76021 Karlsruhe, Germany.

² CEA, DEN, DPC/SEARS/LISL, Bât. 391, F-91191 Gif-sur-Yvette, France.

³ Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark.

E-mail: nicolas.finck@kit.edu

Abstract. Trivalent americium was adsorbed on magnetite and maghemite under similar chemical conditions and the local environment probed by EXAFS spectroscopy. In both samples, partially hydrated Am(III) binds the surface but slightly different surface complexes were identified. On Fe₃O₄, Am(III) forms monomeric tridentate surface complexes similar to that reported for Pu(III) at the (111) surface. In contrast, the lower number of detected Fe atoms may suggest that Am(III) forms monomeric bidentate surface complexes on γ -Fe₂O₃. Alternatively, the lower Fe coordination number can also be due to the presence of vacancies in maghemite. XPS data imply very similar binding environments for Am at both Fe oxide surfaces.

1. Introduction

Deep geological disposal of high level nuclear waste (HLW) confined in steel canisters is under consideration in many countries. Over geological time scales, groundwater may reach the canisters and corrode steel. The Fe corrosion products may in turn interact with radionuclides leached out of the HLW matrix, and this process is of considerable interest. Earlier steel corrosion experiments performed in the laboratory under simulated repository conditions showed the formation of various iron (hydr)oxide phases as corrosion products. Among them, magnetite (Fe₃O₄) has been frequently detected, and upon partial oxidation was found to partly transform into isostructural maghemite (γ -Fe₂O₃) [1]. The neoformation of such secondary phases represents a significant retention potential for the long lived and radiotoxic actinides (An). Structural incorporation and surface adsorption are relevant long term retention modes.

As reducing conditions are expected in deep geological HLW repositories, notably due to the very low redox potential established by steel corrosion, An may prevail in lower oxidation state(s). Several sorption studies of An on magnetite have been reported. U(VI) [2] contacting pre-formed Fe₃O₄ is (partly) reductively immobilized whereas only little U(VI) reduction occurs upon interaction with γ -Fe₂O₃. Also, irrespective of the addition as Pu(V) or Pu(III), only highly specific Pu(III) surface complexes form on magnetite [3]. However, no comparative sorption study of trivalent actinides with both Fe₃O₄ and γ -Fe₂O₃ has been reported so far. The goal of this study is to elucidate the adsorption



mechanism of trivalent An, using Am(III) as representative, on either magnetite or maghemite under comparable chemical conditions by probing the Am L_3 -edge by X-ray absorption spectroscopy (XAS).

2. Experimental

All experiments were performed under anoxic conditions (Ar glove box). Magnetite and maghemite were prepared as described elsewhere [2]. The sorption samples were prepared by adding Am(III) to either magnetite (sample AmAdsMagn) or maghemite (sample AmAdsMagh) under constant stirring, and similar chemical conditions were considered: $[Am]_{\text{initial}} = 20 \mu\text{mol/L}$, $2.5 \text{ g/L Fe}_3\text{O}_4$ or $\gamma\text{-Fe}_2\text{O}_3$, 0.1 mol/L NaCl . After 2 days, pH and E_h (vs S.H.E.) were measured in suspension: pH = 9.7 ± 0.1 and $E_h = -0.071 \pm 30 \text{ mV}$ for AmAdsMagn and pH = 9.9 ± 0.1 and $E_h = +0.301 \pm 30 \text{ mV}$ for AmAdsMagh. The Am and Fe concentrations in the supernatants were determined by HR-ICP-MS (Thermo Element XR) after ultra-centrifugation for 1 hour at $694,000 \text{ g}$ (Beckman XL-90). In both samples the Am concentration was $< 5 \cdot 10^{-11} \text{ mol/L}$ and the Fe concentration was $< 2 \cdot 10^{-8} \text{ mol/L}$.

The Fe oxides were characterized by X-ray diffraction (XRD) with a D8 Advance diffractometer using Cu-K α radiation and an energy-dispersive (Sol-X) detector (Bruker). Fits (Rietveld method) to the XRD data were provided by the TOPAS 4.2 software (Bruker). The solids were further analyzed by scanning electron microscopy (SEM) with an ESEM Quanta 650 FEG (FEI) and the specific surface area was determined by the Brunauer-Emmett-Teller (BET) method [4] using N₂ adsorption with an AUTOSORB-1 (Quantachrome Corporation). Information on the valence states of Fe and adsorbed Am in the sorption samples was provided by X-ray photoelectron spectroscopy (XPS) analysis with a VersaProbe II (ULVAC-PHI).

Am L_3 -edge EXAFS spectra were collected at the INE-Beamline [5] for actinide science at the ANKA Synchrotron Radiation Facility (Karlsruhe, Germany). The energy calibration was done by assigning the first inflection point of a Zr foil at 17998 eV and this reference was measured in parallel with the samples. Data were collected in fluorescence mode using a 5-element low energy germanium solid state detector (Canberra-Eurisys). Data analysis was performed by using Athena and Artemis interfaces to the Ifeffit software [6] following standard procedures [7], with an amplitude reduction factor of $S_0^2 = 0.88$.

3. Results and discussion

3.1. Solid phases characterization

Scanning electron micrographs showed that Fe_3O_4 particles have octahedral shapes and sizes ranging from ~ 50 to 400 nm (Figure 1). Maghemite was obtained by oxidation of magnetite and has similar size and shape as the precursor, in agreement with [1]. Thus, Fe(II) oxidation to form $\gamma\text{-Fe}_2\text{O}_3$ only marginally affected particle morphology and size. According to the XRD analysis (Figure 2) magnetite (cubic, $Fd3m$) contains marginal amounts ($\sim 2 \%$) of cubic maghemite even though it was stored under anoxic conditions as a suspension (prepared well in advance). Note that the very low amount of maghemite is close to the XRD detection limit and it may likely originate from Fe(II) leaching during magnetite purification by dialysis (several weeks). This minor amount is not expected to significantly affect the sorption studies. Maghemite consists of $78 \pm 2 \%$ cubic and $22 \pm 2 \%$ tetragonal $\gamma\text{-Fe}_2\text{O}_3$, meaning that the cubic magnetite structure is preserved upon oxidation, with vacancies created by Fe(II) release. Vacancies ordering leads to a superstructure that can be indexed as tetragonal [1].

The Fe $2p_{3/2}$ XPS spectrum of maghemite ($\gamma\text{-Fe}_2\text{O}_3$), which was obtained by oxidation of Fe_3O_4 ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$), almost overlays that of hematite ($\alpha\text{-Fe}_2\text{O}_3$), meaning that the Fe(II) content in $\gamma\text{-Fe}_2\text{O}_3$ is marginal ($\sim 1.5 \pm 1.5 \%$) (Figure 3). For the Fe_3O_4 used in the sorption study, the shoulder at the low energy side of the Fe $2p_{3/2}$ line, assigned to Fe(II), is of slightly lower intensity than in the fresh sample, indicating some surface oxidation, consistent with XRD data. Accordingly, the Fe(II) content ($28 \pm 3 \%$) is slightly lower than the theoretical value of 33% . Both samples have a similar specific surface area: $13.1 \pm 0.5 \text{ m}^2/\text{g}$ for magnetite and $15.3 \pm 0.5 \text{ m}^2/\text{g}$ for maghemite, consistent with earlier studies [2].

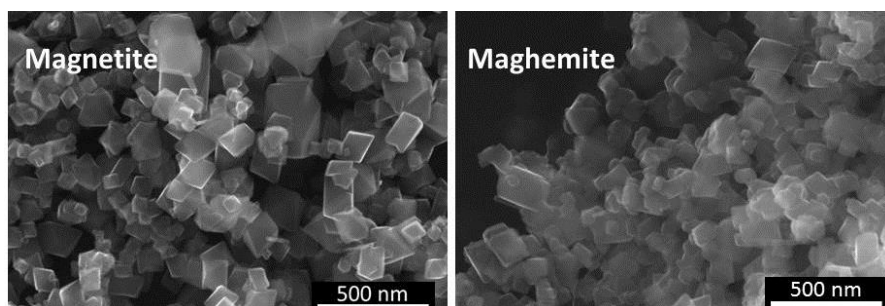


Figure 1. Scanning electron micrographs of the magnetite and maghemite substrates.

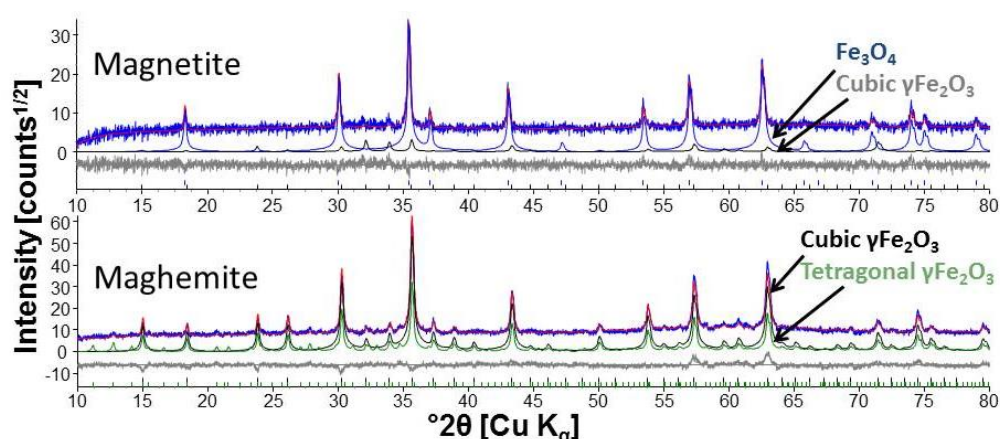


Figure 2. Experimental (blue line) and modeled (red line) XRD data with contribution of each single phase (the grey line represents the residual).

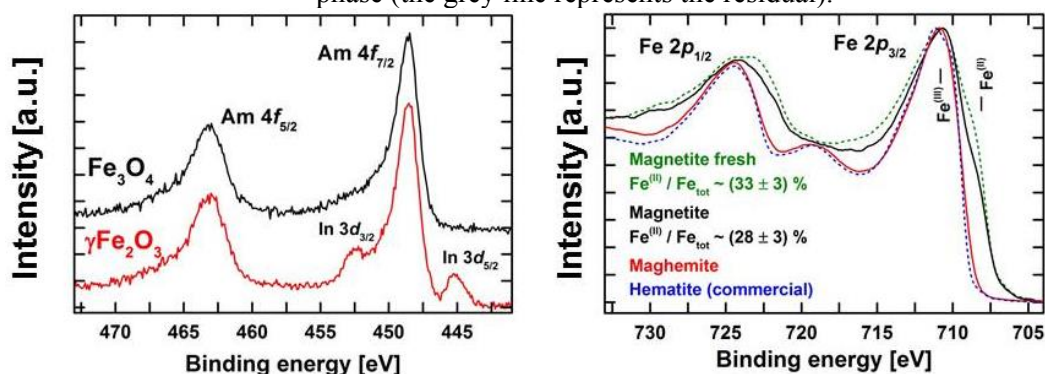


Figure 3. Am 4f (left) and Fe 2p (right) XPS spectra, together with Fe reference compounds (freshly prepared Fe_3O_4 and hematite); spectra are charge referenced to O 1s at 530.0 eV (the In 3d lines originate from the substrate underneath).

3.2. Characterization of Am surface species

According to ICP-MS data, Am is quantitatively retained at the surface of the substrates. XPS was first used to probe the adsorbed actinide (Figure 3). The Am 4f_{7/2} binding energy is identical (448.5 eV) in both samples, suggesting similar binding environments, and is not affected by the difference in substrate composition, i.e., the presence or absence of Fe(II).

EXAFS data of the reference Am(III) aquo ions (in perchloric acid) were recorded first (Figure 4) and could be modeled with one O shell containing $N_{\text{O}1} = 9.0(4)$ atoms at $R_{\text{Am-O}1} = 2.47(1)$ Å (Table 1), which agrees with earlier findings [7]. After contact with magnetite or maghemite, the Am environment changed as indicated by the differences in EXAFS spectra at $k > 6$ Å⁻¹. In the Fourier transforms (FTs) the first peak corresponding to bound O atoms is of lower intensity in the sorption samples, and contributions from neighboring shells are visible at $R + \Delta R \sim 3$ Å and additionally at ~ 2.5

Å in AmAdsMagh. In both samples, the data could be well fit considering two O subshells in the Am first coordination sphere and higher distance Fe backscatterer(s) (Table 1). No neighboring Am could be detected in any sample, ruling out the presence of surface precipitates or polymers.

Table 1. Quantitative EXAFS analysis of the samples

Sample	FT range ^a	Fit range ^b	Path	<i>N</i>	<i>R</i> [Å]	σ^2 [Å ²]	<i>R_f</i> (×10 ³)
Am(III) _{aq}	3.2-10.2	1.7-2.6	Am-O1	9.0(2)	2.47(1)	0.008	3.1
AmAdsMagn	3.3-9.0	1.6-4.1	Am-O1	5.4(3)	2.41(1)	0.003	9.0
			Am-O2	2.5(6)	2.59(1)	0.003	
			Am-Fe1	2.7(3)	3.45(1)	0.006	
			Am-Fe2	0.9(2)	4.09(4)	0.003	
AmAdsMagh	3.3-9.0	1.6-3.7	Am-O1	6.0(2)	2.43(1)	0.004	2.2
			Am-O2	3.0(3)	2.67(1)	0.004	
			Am-Fe1	1.1(3)	3.54(2)	0.006	

^aFourier transformed range, ^b*R* + Δ*R* interval for the fit. *N* is the coordination number, *R* is the interatomic distance, σ^2 is the mean square displacement (“Debye-Waller” term), *R_f* is the figure of merit of the fit as defined in [6].

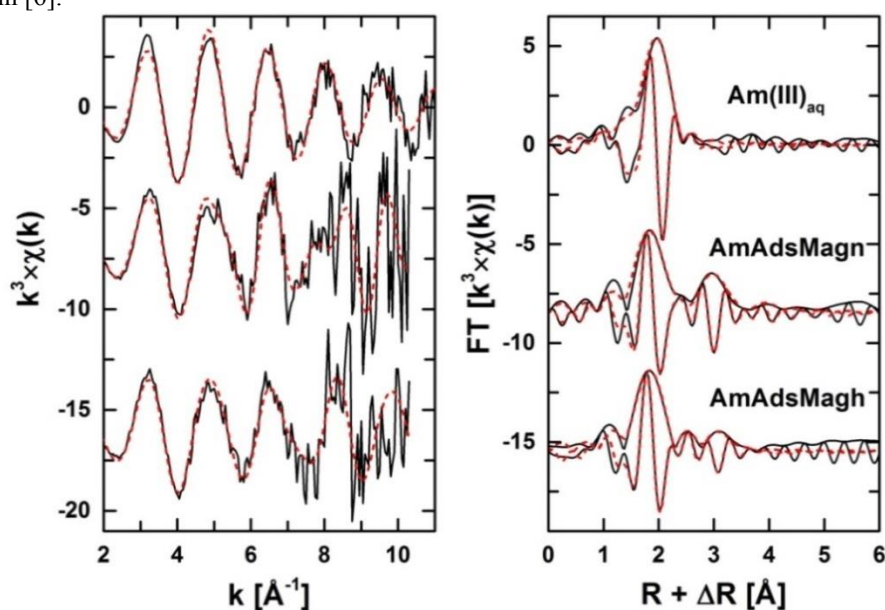


Figure 1. Experimental (solid black line) and modeled (dashed red line) EXAFS spectra (left) and corresponding Fourier transforms (right) of the Am(III) aquo ions and of the sorption samples.

In both samples Am bound to the surface (O2 shell at 2.59-2.67 Å) retains part of its hydration sphere (O1 shell at ~2.42 Å). The detection of 3 Fe atoms at ~3.5 Å in AmAdsMagn is consistent with earlier Pu(III) studies [3], where monomeric tridentate inner-sphere surface complexes at Fe₃O₄ (111) have been reported. Americium thus forms similarly stable complexes on magnetite. SEM evidenced crystals of octahedral shapes where the (111) face predominates and thus sorption at this face certainly dominates, but Am binds also other crystallographic planes in our powder sample. Compared to Fe₃O₄, Am is located at slightly larger distance on γ-Fe₂O₃ (O2 shell at 2.67 Å) and only ~1 Fe atom was detected, hinting at a slightly different binding environment. The AmAdsMagh data can be explained by the formation of monomeric bidentate inner-sphere surface complexes on γ-Fe₂O₃, whereby Am binds two O atoms at the edge of FeO₆ octahedra, even though the O2 shell at 2.67 Å contains 3 atoms. In that configuration, the number of detected Fe is limited, in agreement with fit results. Alternatively, the low number of detected Fe can also be explained by the presence of vacancies in γ-Fe₂O₃.

4. Conclusions

Am(III) was adsorbed onto magnetite and maghemite under similar chemical conditions and the binding environment probed by XAS. Partially hydrated Am(III) is adsorbed on Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, but dissimilar neighboring Fe shells point to slightly different binding sites. For magnetite, the data are consistent with earlier Pu(III) findings, i.e., the formation of monomeric tridentate Am(III) surface complexes. For maghemite, the lower number of Fe atoms detected at larger distances may indicate the formation of monomeric bidentate complexes at the surface or can be due to vacancies in the $\gamma\text{-Fe}_2\text{O}_3$ lattice.

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